Evaluation of energy density as performance indicator for thermal energy storage at material and system levels

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Abstract

The increase of the capacity factor of thermal processes which use renewable energies is closely linked to the implementation of thermal energy storage (TES) systems. Currently, TES systems can be classified depending on the technology for storing thermal: sensible heat, latent heat, and sorption and chemical reactions (usually known as thermochemical energy storage). However, there is no standardized procedure for the evaluation of such technologies, and therefore the development of performance indicators which suit the requisites of the final users becomes an important goal. In the present paper, the authors identified the energy density as an important performance indicator for TES, and evaluated it at both material and system levels. This approach is afterwards applied to prototypes covering the three TES technologies: a two-tank molten salts sensible storage system, a shell-and-tube latent heat storage system, and a magnesium oxide and water chemical storage system. The evaluation of the energy density highlighted the difference of its value at the material value, which presents a theoretical maximum, and the results at system level, which considers all the parts required for operating the TES, and thus presents a significantly lower value. Moreover, the proposed approach captured the effect of the complexity and overall size of the system, showing the relevance of this performance indicator for evaluating technologies for applications in which volume is a limiting parameter.

Keywords: thermal energy storage (TES); energy density; sensible heat; latent heat; chemical reaction; performance indicator

Nomenclature

Dimensional variables

V	Volume [m^3]
T_{max}	Maximum system storage temperature [ºC]
T_{min}	Minimum system storage temperature [ºC]
$T_{melt.high}$	Highest temperature in the melting range [ºC]
$T_{melt.low}$	Lowest temperature in the melting range [ºC]
T_{hyd}	Hydration temperature [ºC]
T_{deh}	Dehydration temperature [ºC]
ΔT_s	Temperature range in solid state [K]
ΔT_{ph}	Temperature range of the phase change [K]
ΔT_l	Temperature range in the liquid state [K]
ΔT_{op}	System operation temperature range [K]
P_{hyd}	Hydration pressure [kPa]
P_{deh}	Dehydration pressure [kPa]
ED	Energy density [$MJ \cdot m^{-3}$]
ESC	Energy storage capacity [MJ]
c_p	Specific heat [$kJ \cdot kg^{-1} \cdot K^{-1}$]
m	Mass [kg]
ΔH_{ph}	Melting enthalpy [$kJ \cdot kg^{-1}$]
$\Delta H^0_{n \to m}$	Reaction enthalpy [$kJ \cdot mol^{-1}$]
M	Molar mass

Non-dimensional variables

n	Hydration state of the highest hydrate
m	Hydration state of the product of the reaction (note n > m)
Δx	Reaction conversion
r	Mass mixing ratio

Greek symbols

ρ	Density [$kg \cdot m^{-3}$]
ρ_{min}	Minimum material density at operation temperature range [$kg \cdot m^{-3}$]

Subscripts

sys	System
comp	Component
mat	Material
l	Liquid
s	Solid
w	Water

1. Introduction

Despite the fact that the scientific community sees renewable energies as one of the main actors of the transition to a new energetic model, these technologies have some drawbacks which might hinder their full implementation worldwide [1]. Hence, energy storage technologies, and especially thermal energy storage (TES), are key factors in order to overcome these drawbacks, with already good examples of available or under-development technologies for building applications [2] and for solar thermal power plants [3]. Nowadays, there are three main technologies for storing thermal energy: sensible heat, latent heat, and sorption and chemical reactions [4]. The principle of sensible heat TES lies on the energy storage as a result of a temperature change in the storage medium. It is the most mature technology with already developed TES systems at commercial level, such as molten salts storage tanks for concentrated solar power (CSP) plants or ice storage for cooling purposes. The latent heat TES technology is based on the phase change of the storage medium, which is able to store more energy than the sensible heat range [1]. Finally, the energy storage based on sorption and chemical reactions (usually known as thermochemical energy storage) consists of reversible physical and chemical processes or reactions involving two substances.

The selection of an adequate TES technology depends on many different parameters, such as the temperature of both the heat sources and heat sinks, the characteristics of the demand, the availability of the source, or the availability of space. The differences between TES technologies and the lack of standardization make the procedure for the selection of the suitable TES technology to become a difficult task. Therefore, in order to carry out a proper cross-comparison among technologies, it is compulsory to define performance indicators, whose relevance strongly depends on the stakeholders involved [5,6]. These indicators, which can be subjective values, measured parameters or qualitative ranks, become an important improvement on the standardization of decision-making strategies, which is reflected in the research work that was previously done in the fields of management and logistics [7-8], construction [9-11], and

energy [12-20], among others. Focusing on the TES technology, Cabeza et al. [21,22] and the International Energy Agency Annex 30 [23] did a first attempt to collect, organise, classify, and compare different performance indicators for such technology in residential and non-residential environments.

A recurrent performance indicator present in TES literature is the energy density, which measures the capacity of the TES material, or system, to store energy in a certain space [24]. This parameter basically depends on the storage process, the medium, and the size of the system. Energy density studies from the literature always show that the TES technology based on sorption and chemical reactions has the highest energy density values (Figure 1), being up to 5 or 10 times higher than latent heat storage [25,26]. However, these values consider energy density only at the material level, without taking into account the temperature range and the complexity of the systems where these TES materials are enclosed (Figure 2), which are known to have an influence on the results. Therefore, the aim of the present paper is to present a methodology to standardize the calculation of the energy density at both material and system levels and, as a consequence, to establish it as a useful performance indicator, or KPI, for the evaluation of the different TES technologies. Furthermore, besides the theoretical formulation, the proposed methodology is applied to three real case studies covering the three different TES technologies.

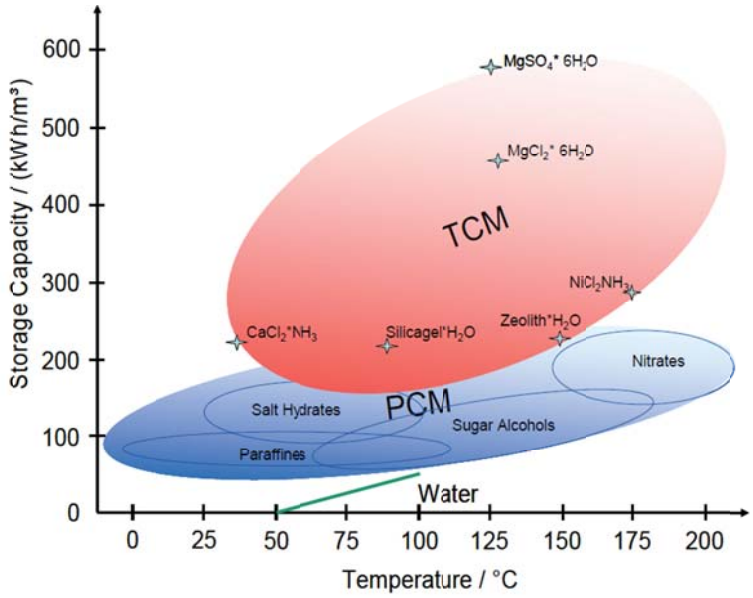

Figure 1. Relation between the storage capacity (or energy density) in front of temperature for the TES technologies based on sensible heat (water), latent heat (PCM), or sorption and chemical reactions (TCM) [25].

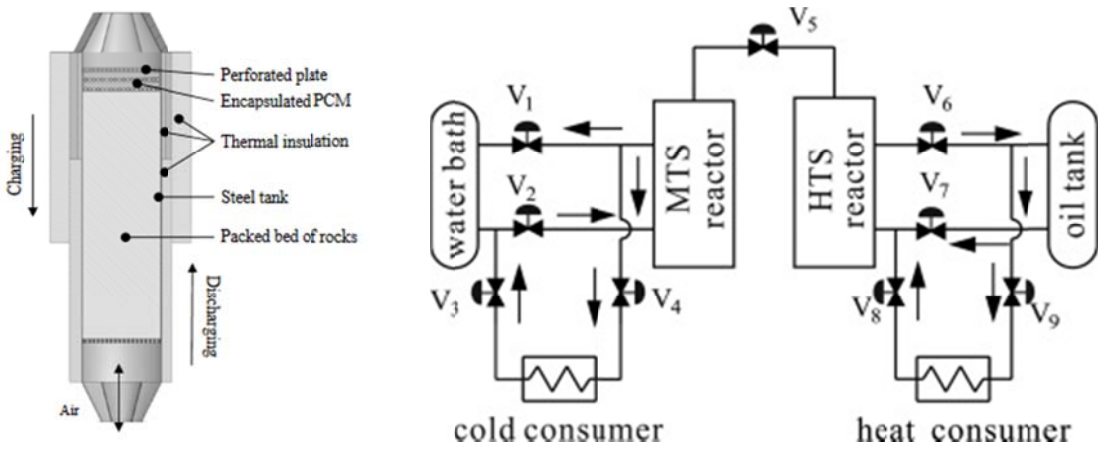

Figure 2. Comparison of TES system complexity. Left: sensible-latent hybrid system [27]; right: sorption TES system [28].

2. General definitions

The approach proposed in this paper uses a specific TES analysis framework and some key concepts. This section defines the general concepts and parameters used in the methodology.

2.1. TES analysis levels

The the analysis of the TES and its integration to applications is carried out according to the levels proposed within the framework of the International Energy Agency Annex 30 [23]. This workspace considers five layers of detail in the analysis, from the process level to the system, sub-system, component, and material levels, as shown in Figure 3.

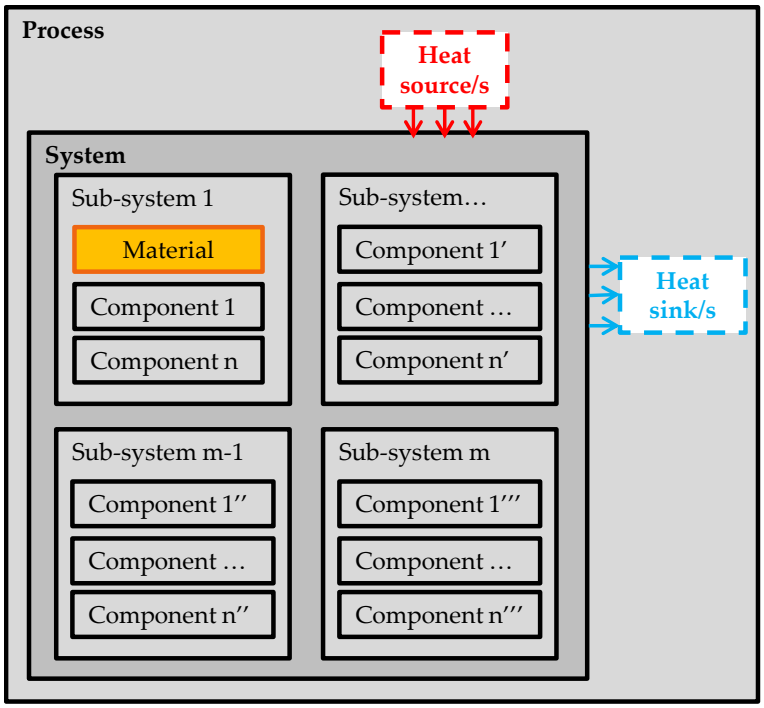

Figure 3. Schematics of the TES analysis levels.

2.2. Energy density

The energy density is a performance indicator that measures the amount of thermal energy that can be stored in a certain space in $J \cdot m^{-3}$, $kWh \cdot m^{-3}$, or any relevant metric prefix. The energy density can be calculated at material level and at system level. The first one takes into account only the properties of the material, while the second one considers the impact of all the components of the system. Moreover, the calculation of this performance indicator depends on the type of material used and the operation conditions of the system, referring always to the maximum storage capacity of the system and considering the ideal conditions in which the system is fully charged and discharged. However, this is not the usual working mode of some sensible and latent heat TES. For example, thermocline storage systems make use of stratification to maintain thermal gradient. This can also be applicable to sensible systems such as molten salts in porous packed bed [29] or systems that can be enhanced with latent heat storage by using a PCM encapsulated packed bed [30]. Similarly, TES based on sorption or chemical reactions can also be influenced by the reaction front, which also creates a gradient in the system [31]. In all these cases the maximum storage capacity is in practice lower than the theoretical maximum. Despite this, the simplification is used to demonstrate the overall concept of the energy density calculation. The case studies are chosen to match this approach.

The methodology presented in this work evaluates two key concepts that determines the calculations at all levels: the operation temperature range and the minimum density.

2.2.1. Operation temperature range (ΔT_{op})

The operation temperature range (ΔT_{op}) is defined by the temperatures at which the system is designed to operate, also referred as nominal conditions. This defines the minimum temperature (T_{min}) and the maximum temperature (T_{max}) at which the material will be maintained during the operation of the system. Systems using the sensible or latent heat TES technologies are considered to be charged or discharged once the material homogeneously achieves either the T_{min} or T_{max}. On the other side, systems using the TES technology based on the sorption and chemical reactions are considered to store only heat in the sorption and chemical reactions processes, and thus the sensible heat is disregarded. In these processes, the charged and discharged status of the system depends only on the completion of the hydration/dehydration or chemical reactions.

2.2.2. Minimum density (ρ_{min})

The density of materials is usually temperature dependant, and thus the volume occupied by such materials might significantly change within the operation temperature range. Moreover, some systems require the material to be porous, stabilized by a matrix, or used in packed bed form, and then the actual volume occupied by the material is bigger than the one that could be estimated with the real density. Considering this, the current methodology considers the minimum density of the material in the operation temperature range of the system, which corresponds to maximum volume occupied. On the other hand, the density of materials for sorption and chemical reactions is also affected by the reaction. Thus, the minimum density is considered as the bulk density of the highest hydrate, always taking into account the porosity or matrixes of the material [26].

3. Methodology

This section describes the equations required to calculate the energy density at material level and the conceptual guide for calculating the energy density at system level for the three storage technologies.

3.1. Material energy density (ED_{mat})

The material energy density (ED_{mat}) considers the storage capacity of the TES material according to its thermo-physical properties and to the operation conditions of the system. The calculation of this performance indicator depends on the storage technology.

3.1.1. Sensible heat TES

The energy density of sensible heat TES materials is calculated with their specific heat, minimum density, and operation temperature range according to Eq. 1:

$$ED_{mat} = c_{p.mat} \cdot \rho_{min.mat} \cdot \Delta T_{op} \quad \text{Eq. 1}$$

where $c_{p.mat}$ is the average specific heat and $\rho_{min.mat}$ the minimum density, both measured in the operation temperature range (ΔT_{op}).

3.1.2. Latent heat TES

The materials for latent heat TES exploit the energy stored during their phase change. However, the operation temperature range for latent systems always cover the sensible region and thus, a part of sensible heat in both phases has to be taken into account. Consequently, the energy density of materials for latent heat TES is measured with the melting enthalpy together with the specific heat at both liquid and solid phases, as shown in Eq. 2:

$$ED_{mat} = \left(c_{p.mat.s} \cdot \Delta T_s + \Delta H_{pc} + c_{p.mat.l} \cdot \Delta T_l\right) \cdot \rho_{min.mat} \quad \text{Eq. 2}$$

where $c_{p.mat.s}$ and $c_{p.mat.l}$ are the average specific heats at the solid and liquid states, respectively, ΔH_{pc} is the melting enthalpy, and $\rho_{min.mat}$ [$kg \cdot m^{-3}$] is the minimum density in the operation temperature range. Additionally, ΔT_s and ΔT_l [K] are the temperature differences in the solid and liquid phases, respectively. Here, ΔT_s is the difference between the minimum temperature in the operation temperature range (T_{min}) and the lowest temperature in the phase change temperature range, while ΔT_l represents the difference between the highest temperature in the phase change temperature range and the maximum temperature in the operation temperature range (T_{max}). Note that these parameters together with the phase change range (ΔT_{pc}) make for the operation temperature range, as shown in Eq. 3. Moreover, the phase change range might be affected by the hysteresis of the material, and consequently, the energy density is calculated with either the temperatures of the heating or the cooling.

$$\Delta T_{op} = \Delta T_s + \Delta T_{pc} + \Delta T_l \quad \text{Eq. 3}$$

3.1.3. TES based on sorption and chemical reactions

Donkers et al. [32] did an attempt of proposing a definition for the calculation of the material energy density in TES systems based on sorption and chemical reactions. They considered an open system with a single reaction and a single heating step, and the reference density was the crystal density of the highest hydrate. In the present study, the calculation of the ED_{mat} for sorption and chemical reactions is done modifying the equations proposed by Donkers et al. [32] in order to implement the concept of minimum density, in concordance to the previous sections, as shown in Eq. 4.

$$ED_{mat} = \frac{|\Delta H^0_{n\to m}| \cdot (n-m)}{M_n} \cdot \Delta x \cdot r \cdot \rho_{min.mat} \quad \text{Eq. 4}$$

where $\Delta H^0_{n\to m}$ is the reaction enthalpy, M_n [kg·mol^{-1}] is the molar mass of the highest hydrate, $\rho_{min.mat}$ is the minimum density, Δx [-] is reaction conversion, r [-] is the mass mixing ratio and it is defined as the ratio between the mass of the highest hydrate and the mass of the material (Eq. 5)

$$r = \frac{m_{\mathrm{n}}}{m_{\mathrm{mat}}} \quad \text{Eq. 5}$$

Despite taking as reference an open system with a single reaction and a single heating step, the current methodology can also be applied in closed systems and in processes with different heating steps that result in multiple reactions. The differences are:

- In closed systems, the volume of the condensed water must be considered when evaluating the volume of the overall system.
- In processes with different heating steps that result in multiple reactions, the methodology follows the recommendation of Donkers et al. [32].

3.2. System energy density (ED_{sys})

The system energy density (ED_{sys}) is a parameter that measures the ratio between the amount of heat that a system can store and the space it occupies. In order to calculate it, two main parameters are required: the system energy storage capacity (ESC_{sys}) and the system volume (V_{sys}). Implementing these two parameters, the ED_{sys} is calculated according to Eq. 6.

$$ED_{sys} = \frac{ESC_{sys}}{V_{sys}}$$ Eq. 6

3.2.1. System energy storage capacity (ESC_{sys})

The ESC_{sys} estimates the total amount of heat that a system can store at nominal conditions. On one hand, it considers the storage capacity of the material according the methodology presented for the ED_{mat}. On the other hand, it takes into account the sensible heat that can be stored in the components that are in contact with the TES material during the charge and that can be recovered by the system during the discharge. Eq. 7 presents how the ESC_{sys} is calculated:

$$ESC_{sys} = ESC_{mat} + ESC_{comp}$$ Eq. 7

where energy storage capacity of the material (ESC_{mat}) is calculated as shown in Eq. 8, while the energy storage capacity of all components of the system (ESC_{comp}) is calculated as shown in Eq. 9:

$$ESC_{mat} = ED_{mat} \cdot \frac{m_{mat}}{\rho_{min}}$$ Eq. 8

$$ESC_{comp} = \sum_{1}^{x} \left(c_{p.comp.x} \cdot m_{comp.x}\right) \cdot \Delta T_{op}$$ Eq. 9

The temperature, mass and specific heat of the components might be difficult to determine, and therefore the calculation procedure of the energy storage capacity of the components (ESC_{comp}) might represent a challenging work due to their diverse nature and complexity. In order to facilitate the standardization of the process, a guideline for determining which components must be taken into account in the calculation is presented below:

- In case of the TES technology based on chemical and sorption reactions in which the reaction pair is stored at ambient temperature, the components do not contribute to the energy storage capacity of the system.
- In all other cases:
    - If the material is not stored always in the same vessel, but moved from one vessel to another during the charge/discharge, the components do not contribute to the energy storage capacity of the system

- If the material is always kept in the same vessel, only the components which are totally or partially immersed (i.e. pumps, sensors, heaters, …) in the material should be considered. Immersed is considered to be in contact with or completely surrounded by the material.
    - For partially immersed components only the mass of the parts completely immersed in the material are taken into account.
    - The exchange of thermal energy between the material and the storage vessel is not considered, therefore the vessel is not taken into account in the calculation.

This methodology assumes that all the components contributing to the energy storage capacity of the system (ESC_{sys}) are kept at the same temperature of the material, no matter what their real temperature is, and thus the energy storage capacity of the components (ESC_{comp}) is measured according to the operation temperature range (ΔT_{op}). In the case that a component is made of elements of different nature, the calculation of its specific heat ($c_{p.comp.x}$) is performed as follows:

- In case that the specific heat and mass of the different elements of the component are known, the $c_{p.comp,x}$ is calculated as the weighted average.
- In case the specific heat and mass of the different elements of the component are not known, the c_p of the most representative part is taken as the $c_{p.comp}$.

3.2.2. System volume (V_{sys})

The V_{sys} represents de total space occupied by the system, measured in terms of physical volume of its parts. It is calculated by taking into account the volume enclosed by the shape of the outer surface of the sub-systems, considering the insulation. This approach assumes the system to be a completely compact solid, where cavities are disregarded. Thus, not all components contribute to the V_{sys}, as some might be placed inside other components.

4. Case studies

The proposed methodology was applied to three real TES systems, covering the three different storage technologies: sensible, latent, and sorption and chemical reactions. Both sensible and latent heat TES technologies were evaluated in a pilot plant from the University of Lleida, Spain [34] (Figure 4), while the TES technology based on sorption and chemical reactions was evaluated in a prototype for sorption storage belonging to Tokyo Institute of Technology, Japan [35-37] (Figure 5).

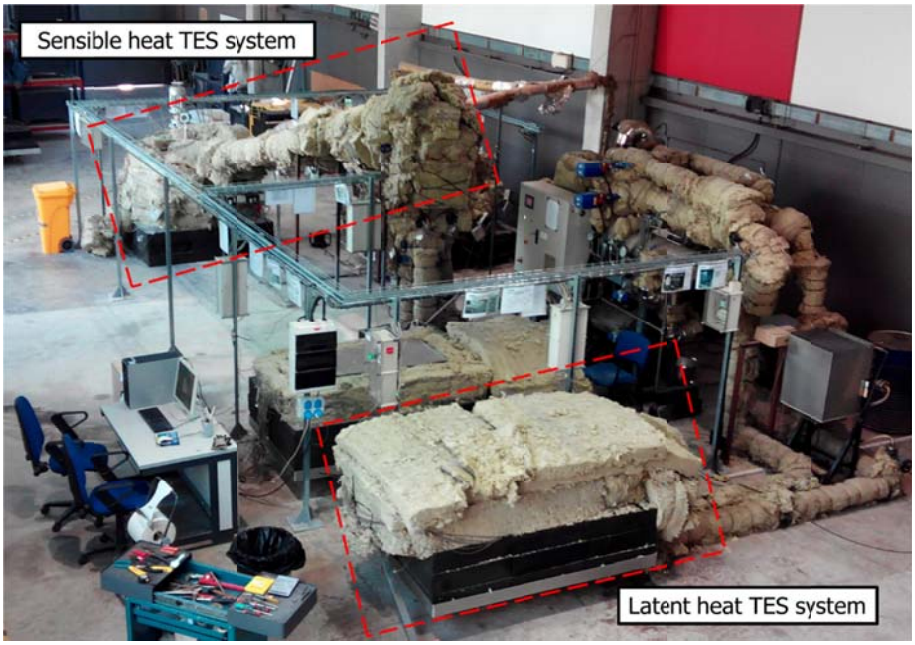

Figure 4. Pilot plant facility at the University of Lleida, Spain.

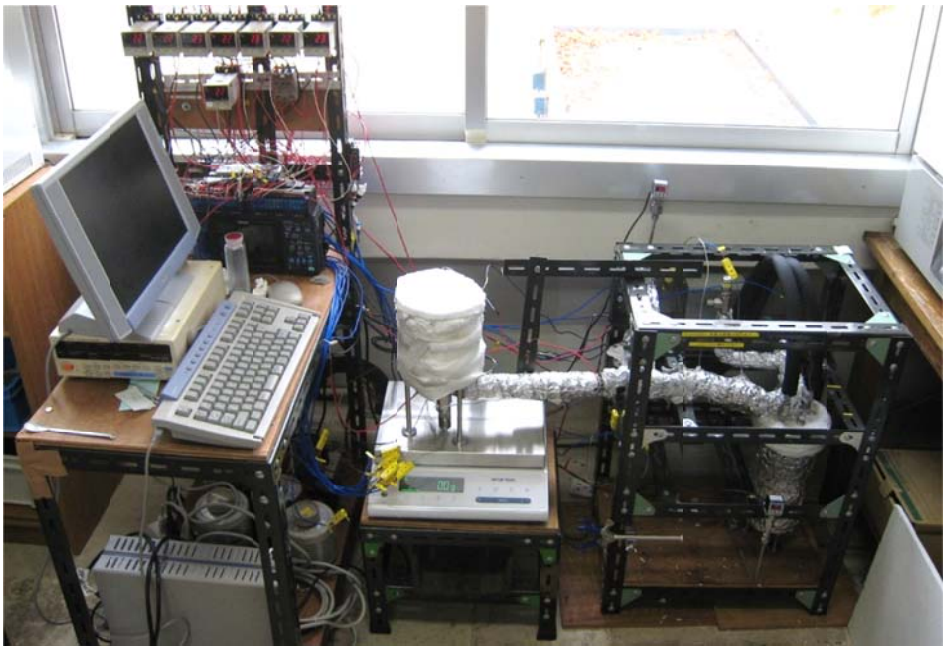

Figure 5. Experimental facility at the Tokyo Institute of Technology, Japan.

4.1. Sensible heat TES

The sensible heat TES technology is evaluated in a scaled two-tank molten salts storage system [33]. It is formed by two 0.57 m^3 tanks containing a total amount of 581 kg of material (Figure 4). The tanks are connected through a salts-heat transfer fluid heat exchanger, which is coupled

to the heat source and the heat sink simulating a CSP plant. The material used is molten salts, which consists of a binary eutectic mixture of 60 wt.% of sodium nitrate ($NaNO_3$) and 40 wt.% of potassium nitrate (KNO_3). The thermo-physical properties of the material are obtained from Peiró et al. [38] for the operation temperature range of the system.

4.2. Latent heat TES

The latent heat TES technology is evaluated in a 0.154 m^3 storage tank based on the shell-and-tube heat exchanger concept which is connected to a heat source and a heat sink simulating the waste heat recovery of an industrial process [39]. The material used is 99.5 kg of high density polyethylene (HDPE).

4.3. TES based on sorption and chemical reactions

The TES technology based on sorption and chemical reactions is evaluated in a prototype using the expanded graphite-magnesium hydroxide ($Mg(OH)_2$) chemical reaction in a closed loop (Eq. 10). The prototype consists of a $2.2 \cdot 10^{-6}$ m^3 cylindrical-shaped packed bed reactor operating containing 49.1 g of material (88.8 % of $Mg(OH)_2$ and 11.2 % of expanded graphite for thermal conductivity enhancement) and a water reservoir. They are connected by heated tubes and stop valves to a heat source and a heat sink simulating the waste heat recovery of an industrial process or the load levelling in thermal power stations [35, 36].

$$\mathrm{MgO(s)} + \mathrm{H_2O} \rightleftarrows \mathrm{Mg(OH)_2}(s) \quad \Delta H = -81.0\ \mathrm{kJ\ mol^{-1}} \qquad \text{Eq. 10}$$

5. Results

5.1. Sensible heat TES

The boundary between the system and the process are the valves that connect the heat source and the heat sink to the system, as shown in Figure 6. The system is divided in three sub-systems: the heat exchange sub-system, the storage sub-system, and the pressurisation sub-system. The heat exchange sub-system contains the heat transfer fluid-molten salts heat exchanger, different valves and the piping. The storage sub-system is composed of two storage tanks. Finally, the pressurisation sub-system introduces N_2 into the storage tanks to reduce the amount of oxygen, and thus reduce the corrosion between the material and the stainless-steel of the tank.

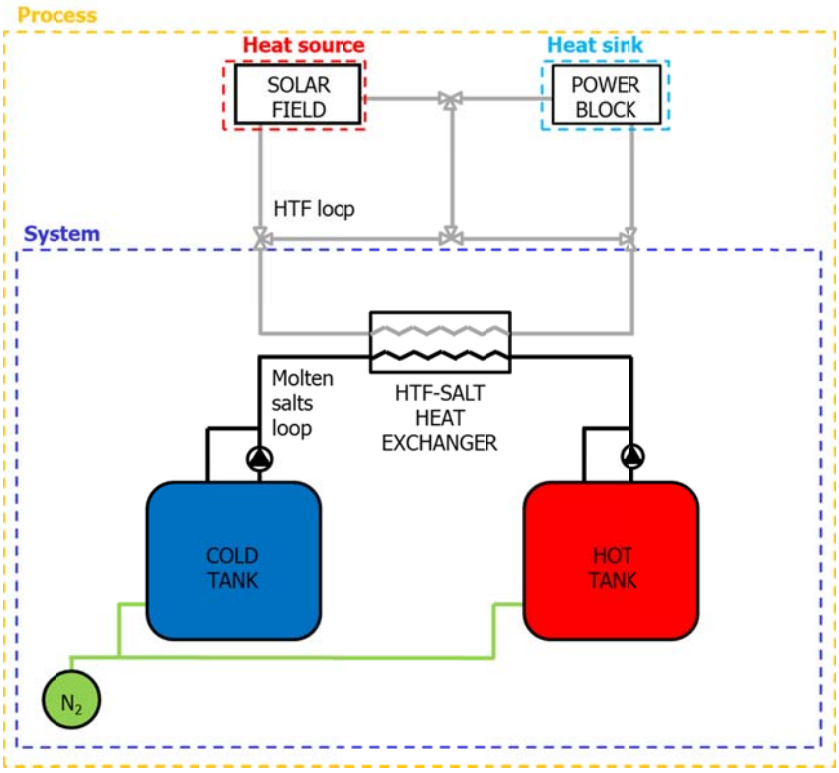

Figure 6. Diagram of the two-tank molten salts (sensible heat) TES system boundaries

5.1.1. Calculation of ED_{mat}

The characteristics of the process define the requirements of the system. On one side, the maximum output temperature of the heat source is 380 ºC. On the other side, the steam turbine of the power block has a minimum operation temperature of 260 ºC. As a result, the operation temperature range (ΔT_{op}) of the system is 120 K. According to this parameter, Table 1 summarizes the data and the final result for the calculation of the material energy density according to Eq. 1.

Table 1. Summary of the sensible heat TES material properties [33], parameters and the ED_{mat}.

Parameter	Value	Units	Parameter	Value	Units
T_{max}	380	ºC	$c_{p.mat}$	1.655	$kJ \cdot kg^{-1} \cdot K^{-1}$
T_{min}	260	ºC	$\rho_{min.mat}$	1346	$kg \cdot m^{-3}$
ΔT_{op}	120	K	**ED_{mat}**	**267.32**	**$MJ \cdot m^{-3}$**
m_{mat}	580.7	kg		**74.25**	**$kWh \cdot m^{-3}$**

5.1.2. Calculation of ED_{sys}

The calculation of the system energy density requires obtaining the energy storage capacity of both the material and components, as well as the volume of the system. The energy storage capacity of the material (ESC_{mat}) is obtained with the parameters presented in Table 1. For the evaluation of the energy storage capacity of the components (ESC_{comp}) the identification of all components and their influence to the final result is needed. In the present study, none of the components contributes to the component energy storage capacity, as the material is moved from one storage tank to the other during the charging and discharging processes and therefore, the heat accumulated in the components cannot be recovered. Finally, the calculation of system volume is shown in Table 2. The final result of the system energy density being (ED_{sys}) is presented in Table 3.

Table 2. Summary of the volume of the different components for the calculation of the final volume of the system (V_{sys}).

Sub-system	Component	Volume
Heat exchange	Heat exchanger + insulation	0.507 m^3
	Piping + insulation	2.043 m^3
	Total	2.550 m^3
Heat storage	Storage tanks + insulation	3.477 m^3
	Base	3.600 m^3
	Total	7.077 m^3
Pressurization	N_2 tank	0.106 m^3
	N_2 pipes	0.003 m^3
	Total	0.109 m^3
	TOTAL (V_{sys})	9.736 m^3

Table 3. Data for calculation of ESC_{sys} and ED_{sys} for the sensible heat TES system.

Parameter	Value
ESC_{comp}	0 MJ
ESC_{mat}	115.33 MJ
ESC_{sys}	115.33 MJ
	32.04 kWh
V_{sys}	9.74 m^3
ED_{sys}	11.85 $MJ \cdot m^{-3}$
	3.29 $kWh \cdot m^{-3}$

5.2. Latent heat TES

The boundary between the system and the rest of the process are the valves at the inlet and outlet of the TES system, which connect the system to the heat source and the heat sink (Figure 7). The latent heat TES system is based on the shell-and-tube heat exchanger concept, and thus the main components are the vessel, the tubes bundle, the manifolds, the separators, and the temperature sensors.

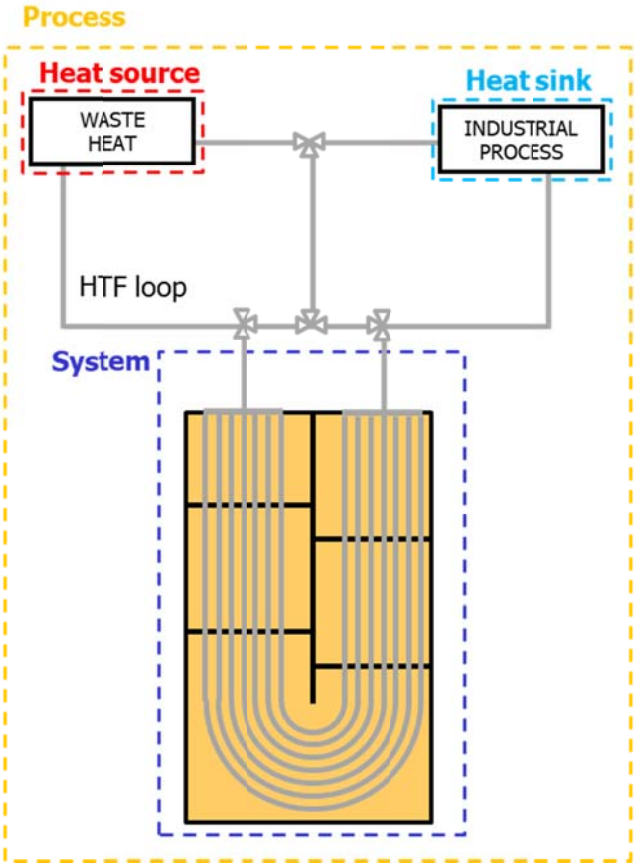

Figure 7. Shell-and-tube latent heat TES system boundaries.

5.2.1. Calculation of ED_{mat}

In this case the process was constrained by a maximum temperature of 155 ºC, which was imposed by the limits of the heat source, and a minimum temperature of 105 ºC, which was required by the heat sink. Hence, the operation temperature range was 50 ºC. The summary of the data and results of material energy density are shown in Table 4.

Table 4. Summary of the latent heat TES material properties [39], parameters and the ED_{mat}.

Parameter	Value	Units	Parameter	Value	Units
T_{max}	155	ºC	m_{mat}	99.5	kg
$T_{melt.high}$	134	ºC	$c_{p.mat.s}$	2.6	$kJ \cdot kg^{-1} \cdot K^{-1}$
$T_{melt.low}$	124	ºC	ΔH_f	138	$kJ \cdot kg^{-1}$
T_{min}	105	ºC	$c_{p.mat.l}$	2.7	$kJ \cdot kg^{-1} \cdot K^{-1}$
ΔT_l	21	K	$\rho_{min.mat}$	785.7	$kg \cdot m^{-3}$
ΔT_{pc}	10	K	**ED_{mat}**	**191.79**	**$MJ \cdot m^{-3}$**
ΔT_s	19	K		**53.27**	**$kWh \cdot m^{-3}$**
ΔT_{op}	50	K			

5.2.2. Calculation of ED_{sys}

The energy storage capacity of the material (ESC_{mat}) is obtained with the parameters presented in Table 4. As above-mentioned, the material is stored during both charging and discharging processes at the same tank, and unlike the previous study case, the energy storage capacity of the components is not null. The components of the system are the storage vessel, the tubes bundle, the separators and the temperature sensors. According to the methodology presented in section 3.2.1, only the tubes bundle and the separators are considered to contribute to the components energy storage capacity (ESC_{comp}), whose values are summarized Table 5.

Table 5. Summary of the results of the ESC_{comp} for the latent heat TES system.

Component	Mass [kg]	Specific heat [$kJ \cdot kg^{-1} \cdot K^{-1}$]	ΔT_{op} [K]	ESC_{comp} [MJ]
Tubes bundle	109.62	0.53	50	2.90
Separators	12.01	0.53	50	0.32
			TOTAL	3.22

The calculation of the system volume for the latent heat storage case is easier than the previous case since the shape of the system, considering both the storage tank and the insulation, can be assimilated to a rectangular parallelepiped with a volume of 1.33 m^3. Finally, the calculation of the system storage capacity (ESC_{sys}) and its energy density (ED_{sys}) is presented in Table 6.

Table 6. Data for calculation of ESC_{sys} and ED_{sys} for the latent heat TES system.

Parameter	Value
ESC_{comp}	3.22 MJ
ESC_{mat}	24.36 MJ
ESC_{sys}	27.58 MJ
	7.66 kWh
V_{sys}	1.33 m^3
ED_{sys}	20.74 $MJ \cdot m^{-3}$
	5.76 $kWh \cdot m^{-3}$

5.3. TES based on sorption and chemical reactions

The boundary between the system and the process are the valves that connect the heat sources and the heat sinks to the system, as shown in Figure 8. The system is divided in two sub-systems: the heat storage sub-system and the water storage sub-system. The heat storage sub-system contains a heat exchanger, the packed bed, the stop valve and the piping, while the water storage sub-system contains a heat exchanger, a water reservoir and piping.

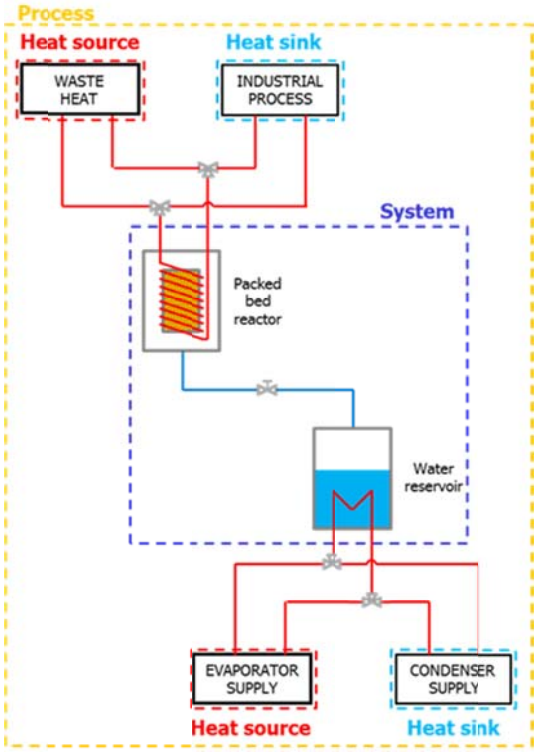

Figure 8. Diagram of the MgO/H_2O chemical TES system.

5.3.1. Calculation of ED_{mat}

The characteristics of the dehydration/hydration constrains the maximum dehydration temperature at 400°C under a water vapor pressure of 2.3 kPa and the minimum hydration temperature at 240°C under a water vapor pressure of 361 kPa. The summary of the data and results of the material energy density are shown in Table 7.

Table 7. Summary of the material properties [35], parameters and the ED_{mat} value.

Parameter		Value	Units	Parameter	Value	Units
T_{min}	T_{hyd}	240	ºC	$\rho_{min.mat}$	714	$kg \cdot m^{-3}$
P_{max}	P_{hyd}	361	kPa	ΔH	-81.0	$kJ \cdot mol^{-1}$
T_{max}	T_{deh}	400	ºC	r	0.888	-
P_{min}	P_{deh}	2.3	kPa	Δx	0.56	-
M_n	$M_{Mg(OH)2}$	58.3	$g \cdot mol^{-1}$	**ED_{mat}**	**494**	**$MJ \cdot m^{-3}$**
m_n	$m_{Mg(OH)2}$	49.1	g		**137**	**$kWh \cdot m^{-3}$**

5.3.2. Calculation of ED_{sys}

The energy storage capacity of the material (ESC_{mat}) is obtained with the parameters presented in Table 7. According to the methodology proposed in section 3.2.1, none of the components contributes to the component energy storage capacity (ESC_{comp}). For the calculation of the volume of the system, the results are summarized in Table 8. Finally, the calculation of the system storage capacity and its energy density is presented in Table 9.

Table 8. Summary of the volume of the different components for the calculation of the final volume of the system (V_{sys}).

Sub-system	Component	Volume
Heat storage	Reactor	$6.877 \cdot 10^{-5}\ m^3$
	Piping + stop valve	$6.877 \cdot 10^{-6}\ m^3$
	Total	$7.565 \cdot 10^{-5}\ m^3$
Water storage	Water reservoir	$1.480 \cdot 10^{-5}\ m^3$
Insulation		$2.304 \cdot 10^{-3}\ m^3$
TOTAL (V_{sys})		$2.395 \cdot 10^{-3}\ m^3$

Table 9. Data for calculation of ESC_{sys} and ED_{sys} for the chemical TES system.

Parameter	Value
ESC_{comp}	0 MJ
ESC_{mat}	$3.397 \cdot 10^{-2}$ MJ
ESC_{sys}	$3.397 \cdot 10^{-2}$ MJ
	$9.436 \cdot 10^{-3}$ kWh
V_{sys}	$2.395 \cdot 10^{-3}$ m^3
ED_{sys}	**14.18 MJ m^{-3}**
	3.938 kWh·m^{-3}

6. Discussion

The energy density at material and system levels was calculated for three real case studies evaluating the three different TES technologies, and their results are summarized in Table 10. These results show the importance of taking into account the complexity and actual size of the system, obtaining a decrease of one order of magnitude between the material and system levels.

The effect of the system complexity is mainly observed in the evaluation of the sensible heat TES system and the latent heat TES system. While the first one presents higher energy density at material level, it shows a lower value at system level. This is caused by the two-tank layout, which has more components than the compact shell-and-tube heat exchanger module from the latent heat storage. It should be also taken into account that the three case evaluated are prototypes, which is translated to a lower storage capacity and overall volume than those expected for actual cases. The low values of the overall volume result into the fact that some components of the system have a very high contribution to the system volume, as downscaling limitations exist for standard components. This is especially relevant for insulation, as the prototypes used the same thickness as real cases. Thus, insulation represents 46%, 86%, and 96% of the overall volume of the system for the sensible heat storage, latent heat storage, and chemical storage systems evaluated, respectively. Furthermore, the components of the chemical storage are oversized due to experimental requirements. In a real set-up, the volume of the heat exchanger and valves was expected to be 10% of the reactor volume, while the water reservoir used for experimentation is 100 times bigger than needed in order to have stable evaporation temperatures. Therefore, an estimation of the effect of the oversizing of components is considered in Table 10, in which the volumes of the systems and the energy densities is also presented without taking into account insulation. Results show a considerable increase in the system energy densities once removing the insulation, which emphasizes the importance of

adequate insulation selection in real cases if energy density is a relevant parameter. Additionally, this increases the differences between technologies, showing a clear lead for chemical storage in terms of system energy density.

On the other side, it is observed that the material energy density results differ from those reported in Figure 1 [25]. Firstly, the energy density of the sensible storage technology presents a higher value than the latent storage technology. As shown in Figure 9, this is mainly caused by the different temperature ranges, which are 120 K and 50 K for the sensible and latent cases, respectively. Moreover, the higher density of molten salts also influences the result, as it benefits the sensible case. However, the slope of the latent curve is steeper, meaning that more energy can be stored in a shorter temperature range. Furthermore, notice that the material energy density in latent heat TES systems increases if sensible heat is considered, as shown in Figure 9. Secondly, the energy density of the TES storage technology based on chemical reactions is below the expected values for thermochemical materials. In this case, the value is reduced because the methodology used in the present research work considers the effects of porosity and pelletizing of the material. These effects reduce the density from around 3600 $kg \cdot m^{-3}$ to 714 $kg \cdot m^{-3}$, from crystal to real values, and therefore greatly affecting the storage capacity of the material.

Nevertheless, the case studies presented work at different temperature ranges, which does not allow for direct comparison of the technologies. On the one hand, each technology will have completely different applications. On the other, a wider temperature range, might yield a better energy density than a system using a shorter range, such in the molten salts two-tank system compared to the HDPE module. However, the latent storage will provide a more stable thermal power due the phase change, which might be desirable in certain applications.

Table 10. Summary of results.

Parameter	Units	Case study		
		Sensible heat TES	Latent heat TES	TES based on chemical reactions
Material	[-]	Molten salts	HDPE	Expanded graphite – $Mg(OH)_2$
Temperature range	[ºC]	260 – 380	105 – 155	240 (discharge) 400 (charge)
$\rho_{min.mat}$	$[kg \cdot m^{-3}]$	1346	785.7	714
ESC_{sys}	[kWh]	32.04	7.66	$9.44 \cdot 10^{-3}$

ED_{mat}	[$kWh \cdot m^{-3}$]	74.25	53.27	137
V_{sys}	[m^{-3}]	9.736	1.33	$2.395 \cdot 10^{-3}$
ED_{sys}	[$kWh \cdot m^{-3}$]	3.29	5.6	3.94
V_{sys} (no insulation)	[m^{-3}]	5.225	0.18	$9.1 \cdot 10^{-3}$
ED_{sys} (no insulation)	[$kWh \cdot m^{-3}$]	6.13	41.86	103.69

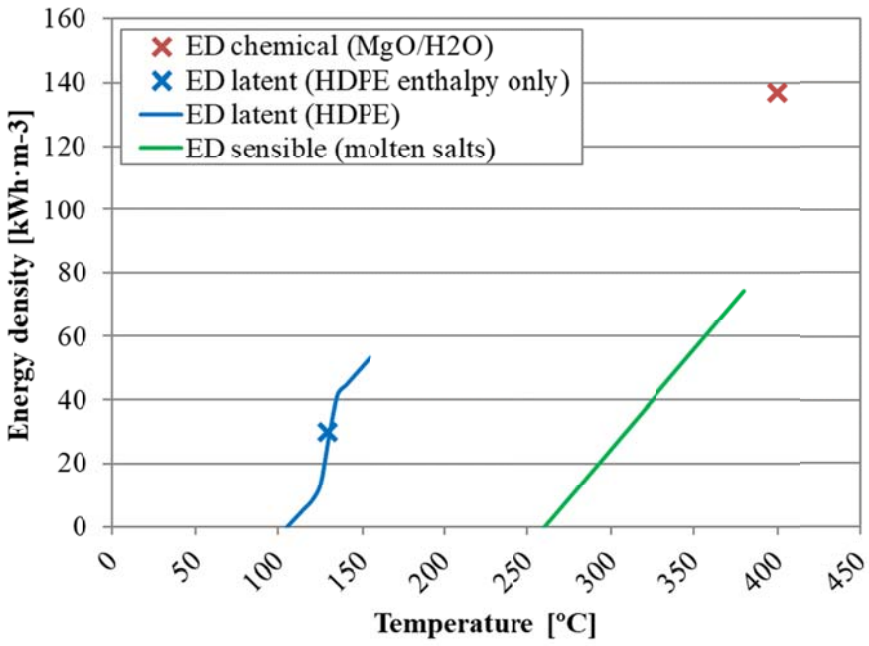

Figure 9. Material energy density depending on temperature range

It is proved that the material energy density is only an indicative of the potential of the technology. Therefore, the layout of the system and all its components should be taken into account since its operation strongly affects the actual energy density of the system. Moreover, the total energy storage capacity of the system as well as its complexity are relevant parts in the calculation. The current paper proposes a calculation method for the volume of the system, considering the space occupied by its components. Nevertheless, the volume of the system is not the space required for its operation, as the system may require safety distances, moving parts, or free areas required for maintenance. Still, these are appliance dependent and not useful for comparing TES technologies.

Another point to take into account is that the material energy storage capacity definition used for the studied cases is not applicable to thermoclines systems or storage based on sorption and chemical reactions with reaction fronts. For these cases, the storage capacity of both the material

and system must consider the temperature gradient [40]. This modification can be introduced in the energy density calculation, although that is beyond the scope of the current research. Nevertheless, the approach of considering the system volume can also be applied to these technologies.

Finally, considering energy density at both material and system level is probed to be useful to evaluate TES systems. These parameters can be especially relevant in applications in which space is limited, and thus where maximizing the storage capacity per volume of the system is a key parameter. In these cases, the energy density would be a key performance indicator of the TES technologies.

7. Conclusions

The energy density of TES systems was evaluated at material and system level. This is applied to three real cases, a sensible storage with a two-tank molten salts sensible heat storage, a latent heat storage with a shell-and-tube heat exchanger containing HDPE, and a chemical energy storage with expanded graphite-magnesium oxide reaction with water (MgO)/H_2O.

Material energy density is usually the reference parameter for studying the potential of TES technologies. However, this might not translate directly into the system energy density, which is strongly affected by its design and operation characteristics.

The complexity of the system, reflected by the components required, and the total energy storage capacity affect the system energy density. Complex systems, such as molten salts storage which requires two storage tanks or closed chemical storages which require water reservoirs, need more components and therefore, the amount of material is comparatively small once taking into account the size of the components. On the other side, the total energy storage capacity defines the overall size of the system, although some components do not scale up proportionally, i.e insulation. Therefore, in small storage capacities the volume of components is proportionally higher, and thus affecting negatively the system energy density.

Finally, the system and material approach for the energy density is probed to be useful for comparing TES technologies. These parameters would be especially relevant in applications in which the volume is limited.

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